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Published in:
Inorganica Chimica Acta

DOI:
10.1016/s0020-1693(97)05605-3

Publication date:
1997

ELSEVIER

Inorganica Chimica Acta 264 (1997) 171–183

Inorganica Chimica Acta

New palladium, platinum and nickel complexes based on rigid phosphorus and nitrogen containing ligands

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Received 13 February 1997; accepted 5 May 1997

Abstract

Three new polydentate phosphorus nitrogen ligands, 1,3-bis[*N,N'*-(2-diphenylphosphino)phenylformimidoyl]benzene (**3**), bis[*N,N'*-(2-diphenylphosphino)phenyl]-1,3-benzenedicarboxamide (**6**) and bis[*N,N'*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide (**7**) with rigid bridging groups have been synthesised. Ligand **7** shows an unexpected large non-bonding P–P coupling of 34 Hz, which can be attributed to the interaction of the lone pairs of the two phosphorus atoms which are directed towards each other due to hydrogen bonding between the two amide hydrogens and the pyridine nitrogen. Complexation experiments with these ligands showed that **3** is a good dinucleating ligand which resulted in the isolation of dichlorodimethyl{1,3-bis[*N,N'*-(2-diphenyl)phosphinophenylformimidoyl]benzene}dipalladium (**8**). In contrast only mononuclear palladium, platinum and nickel complexes have been obtained from ligand **7**. The crystal and molecular structure of dichloro{bis[*N,N'*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}platinum (**9**) was determined by X-ray crystallography. Complex **9** crystallises in the monoclinic space group $C2/c$ with $a=35.547(3)$, $b=9.192(1)$, $c=24.192(2)$ Å, $\beta=102.795(7)°$, $V=7925.3(13)$ Å^3 and $Z=8$; the structure was refined to $R_F=0.031$. This complex has a square planar configuration around platinum, in which the two phosphorus atoms are positioned *trans* to each other. For comparison, mononuclear complex dichlorobis(2-diphenylphosphinoaniline)platinum (**12**) was prepared and the structure elucidated by X-ray analysis. Complex **12** crystallises in a triclinic space group $P\bar{1}$ with $a=10.0692(12)$, $b=10.839(2)$, $c=24.350(5)$ Å, $\alpha=88.042(15)$, $\beta=79.091(14)$, $\gamma=75.518(11)°$, $V=2526.4(8)$ Å^3 and $Z=2$; the structure was refined to $R_F=0.0355$. In platinum complex **12**, a square planar geometry is found but the two phosphines are positioned *cis* to each other, whereas an unusual binding of the chloride anions is observed.

Keywords: Crystal structures; Palladium complexes; Platinum complexes; Nickel complexes; P,N-ligand complexes

1. Introduction

Bidentate ligands with a phosphorus and a nitrogen donor group have attracted considerable interest in homogenous catalysis. These ligands have been proven to be highly effective in nickel catalysed cross coupling reactions [1], carbonylation reactions such as alkoxycarbonylation and polyketone production [2] and in allylic substitution reactions [3]. The unique properties of these ligands are due to a stable phosphorus–metal bond and a relatively labile nitrogen–metal bond. Therefore, they can stabilise metal ions in a variety of oxidation states and form complexes with several geometries [4].

An attractive molecule, from a point of view of reactivity, is 2-diphenylphosphinoaniline, which is air stable and can be synthesised easily and in high yields [5]. Cooper et al. have shown that in complexation with metals (Ni, Pt), the coordinated aromatic amine group can be easily and reversibly deprotonated [6,7].

For sometime, we have been interested in the chemistry of dinucleating nitrogen ligands of type **I** (Fig. 1), which are able to coordinate two copper or two nickel ions [8]. How-

Fig. 1. Polydentate ligands.

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PII S0020-1693(97)05605-3

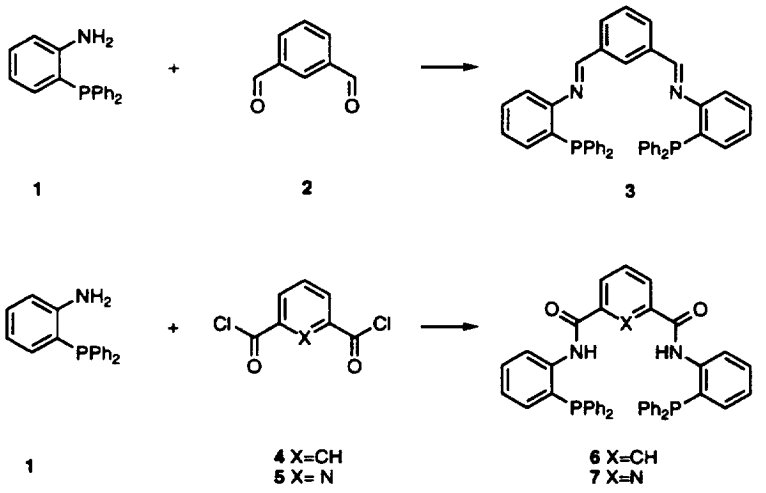
ever, dinucleating nitrogen ligands are less suitable in stabilising Pd(0) and Pt(0) species. Therefore we focused our attention on polydentate PN ligands of type **II** in which two PN units are linked by a rigid bridging group, being either a phenyl or a pyridyl bridge. Here we report the synthesis of iminophoshine and amidophosphine ligands based on 2-diphenylphosphinoaniline and their complexation behaviour with palladium, platinum and nickel. Furthermore, we report the crystal structures of dichlorobis(2-diphenylphosphinoaniline)platinum and dichloro{bis[*N,N'*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}platinum.

2. Results and discussion

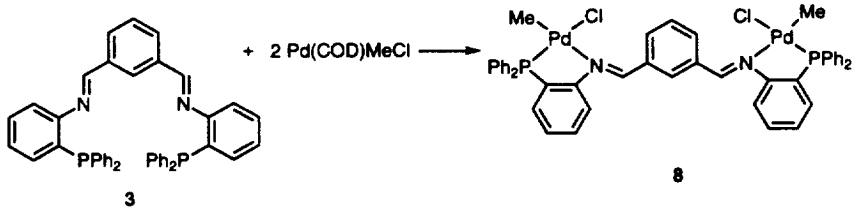
2.1. Synthesis and characterisation

The reaction of 2-diphenylphosphinoaniline [4] (**1**) and isophthalaldehyde (**2**) under Dean–Stark conditions in toluene gave 1,3-bis[*N,N'*-(2-diphenylphosphino)phenylformimidoyl]benzene (**3**) in 77% yield (Scheme 1). ^{31}P NMR showed one absorption at δ −14 whereas ^{1}H NMR showed the characteristic imine proton at δ 8.16. Bis[*N,N'*-(2-diphenylphosphino)phenyl]-1,3-benzenedicarboxamide (**6**) and bis[*N,N'*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide (**7**) were prepared from isophthaloyl dichloride (**4**) and 2,6-pyridinedicarbonyl dichloride (**5**), respectively, in THF in 72 and 54% yields, following a literature procedure for the synthesis of *N,N'*-[2-(diphenylphosphino)phenyl]benzamide [9]. Both ligands showed one absorption in ^{31}P NMR at δ −20. The amide proton in **6** appears as a singlet at δ 8.81 whereas in ligand **7** the amide proton absorption is shifted to lower field, i.e. δ 10.60, which indicates hydrogen bonding of the amide hydrogens to the pyridine nitrogen [10]. In ^{13}C NMR, virtual triplets were obtained for the *ipso*, *ortho* and *meta* carbon of the phenyl rings of the phosphine moiety, which is caused by an unusual large non-binding P–P coupling of 34 Hz. Large P–P couplings are found when the two lone pairs of phosphorus are directed towards each other and the phosphorus nuclei are in close contact [11]. In ligand **7**, hydrogen bonding of the amide hydrogens to the pyridine nitrogen positions the phosphorus atoms close to one another, in such a way that the lone pairs of phosphorus are directed towards each other. This is confirmed by the fact that for ligand **6** no virtual triplets in the ^{13}C NMR spectrum were seen.

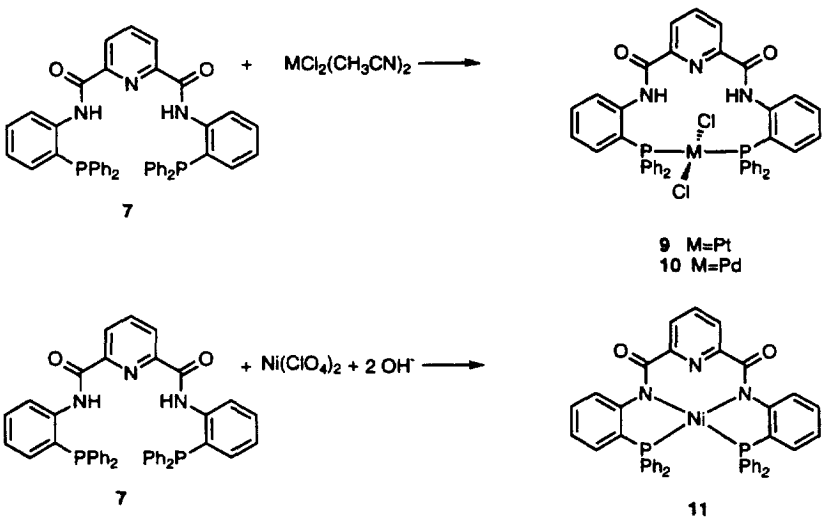
Complexation of ligand **3** with 1 equiv. of $(CH_3CN)_2PdCl_2$ gave several products which unfortunately could not be characterised. Complexation of ligand **3** with 2 equiv. of $(CH_3CN)_2PdCl_2$ in dichloromethane resulted in insoluble material which is probably an oligonuclear complex. Similar observations are frequent for palladium dichloride complexes in which two chlorides bridge two palladium centres in a four centre bond [12]. To prevent the formation of oligonuclear complexes, we used Pd(COD)MeCl (the methyl group does not bridge or function as an anion; COD = 1,5-cyclooctadiene). Complexation of L^1 with 2 equiv. of Pd(COD)MeCl in THF at room temperature resulted in white solid material



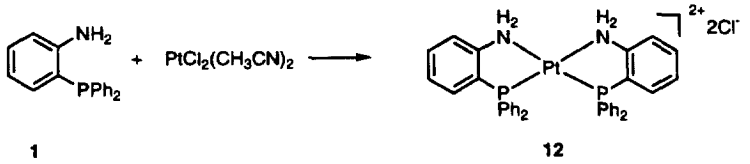
Scheme 1. Synthesis of the ligands.



Scheme 2. Synthesis of dinuclear palladium complex **8**.



Scheme 3. Synthesis of Pd, Pt and Ni complexes of ligand **7**.



Scheme 4. Synthesis of dichlorobis[(diphenylphosphino)benzeneamino]platinum (**12**).

which was crystallised from CH_2Cl_2/pentane (Scheme 2). Elemental analysis and ^{31}P and ^{1}H NMR spectroscopy revealed a dinuclear complex **8**. Analogous to other phosphorus–nitrogen palladium complexes [13], chlorine is expected to be *trans* to phosphorus and the methyl group *trans* to nitrogen due to the *trans* effect [14,2b]. It should be noted that complexation of **3** with 1 equiv. of Pd(COD)MeCl did not lead to the formation of a single well defined mononuclear complex. Reaction of **6** with 1 or 2 equiv. $(CH_3CN)_2PdCl_2$ resulted, according to ^{31}P NMR, in a mixture of products which have not been characterised.

In contrast with the formation of dinuclear complexes of **3**, reaction of **7** with either 1 or 2 equiv. of $(CH_3CN)_2PtCl_2$ in dichloromethane yielded the mononuclear complex dichloro{bis[*N*-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}platinum (**9**) as a bright yellow solid (Scheme 3). Crystallisation from dichloromethane/hexane provided crystals suitable for X-ray analysis. The ^{31}P NMR spectrum of **9** showed a single resonance at δ 15.4 with a ^{2}J coupling to ^{195}Pt of 2457 Hz. This coupling is relatively small due to the fact that the two phosphorus atoms are positioned *trans* to each other [15]. In the ^{1}H NMR spectrum of **9**, the absorption of the amide protons is shifted to δ 11.05. This is due to an extra hydrogen bonding of the amide protons to chlorine, which is also found in the crystal structure (vide infra). In the ^{13}C NMR spectrum, the absorptions of the carbon atoms *ipso*, *ortho* and *meta* to phosphorus were again shown as virtual triplets due to a P–P coupling (via the metal).

For comparison, mononuclear dichlorobis(2-diphenylphosphinoaniline)platinum (**12**) was prepared from 2 equiv. of 2-diphenylphosphinoaniline (**1**) and 1 equiv. $(CH_3CN)_2PtCl_2$ (Scheme 4). This complex showed in the ^{31}P NMR spectrum a single resonance of δ 25.7 with a much larger ^{195}Pt coupling of 3349 Hz indicating that the two phosphorus atoms are coordinating *cis* to each other. Crystals of **12** suitable for X-ray analysis were grown from chloroform/hexane.

Analogous to complex **9**, dichloro{bis[*N*,*N*′-(2-diphenylphosphino)phenyl]-2,6-pyridinecarboxamide}palladium (**10**) was obtained from **7** and $(CH_3CN)_2PdCl_2$ in dichloromethane in 78% yield (Scheme 3). In the ^{31}P NMR spectrum one singlet was obtained at δ 19.4 and the amide proton

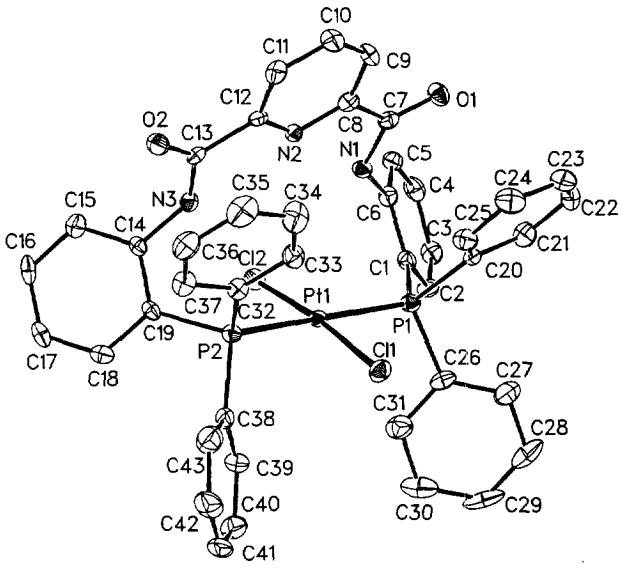


Fig. 2. ORTEP plot of complex **9** with adopted numbering scheme.

amide is less accessible for coordinating to platinum or palladium. For this reason, P,P-coordination is preferred over P,N-coordination for **7** unless deprotonation takes place as observed in complex **11**.

2.2. *X-ray structure of dichloro{bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}-platinum (**9**)*

The crystal structure of **9** together with the adopted numbering scheme is shown in Fig. 2. The crystallographic data, selected bond distances, selected bond angles and atomic coordinates are collected in Tables 1–4.

The structure has a pseudo mirror plane through C(10), N(2), Cl(1), Cl(2) and Pt(1). The platinum ion has a distorted square planar ligand coordination consisting of two phosphorus atoms of the chelating ligand **7** and two chlorines. The deviations of the atoms from the Pt(1), P(1), P(2), Cl(1), Cl(2) least-squares plane are 0.043(1), 0.093(1),

Table 2
Bond distances (Å) for compound **9** (standard deviation in parentheses)

Pt(1)–Cl(1)	2.3174(13)
Pt(1)–Cl(2)	2.3102(12)
Pt(1)–P(1)	2.3212(12)
Pt(1)–P(2)	2.3196(12)
P(1)–C(1)	1.834(5)
P(1)–C(20)	1.830(5)
P(1)–C(26)	1.825(5)
P(2)–C(19)	1.822(5)
P(2)–C(32)	1.822(5)
P(2)–C(38)	1.826(5)
O(1)–C(7)	1.214(6)
O(2)–C(13)	1.220(6)
N(1)–C(6)	1.425(6)
N(1)–C(7)	1.348(6)
N(2)–C(8)	1.337(6)
N(2)–C(12)	1.324(6)
N(3)–C(13)	1.357(7)
N(3)–C(14)	1.414(6)
C(1)–C(2)	1.380(7)
C(1)–C(6)	1.399(7)
C(2)–C(3)	1.397(7)
C(3)–C(4)	1.378(8)
C(4)–C(5)	1.379(8)
C(5)–C(6)	1.387(7)
C(7)–C(8)	1.505(7)
C(8)–C(9)	1.392(7)
C(9)–C(10)	1.379(7)
C(10)–C(11)	1.375(7)
C(11)–C(12)	1.394(8)
C(12)–C(13)	1.510(7)
C(14)–C(15)	1.396(7)
C(14)–C(19)	1.400(6)
C(15)–C(16)	1.374(7)
C(16)–C(17)	1.390(7)
C(17)–C(18)	1.390(7)
C(18)–C(19)	1.394(7)
C(20)–C(21)	1.390(7)
C(20)–C(25)	1.378(7)
C(21)–C(22)	1.377(8)
C(22)–C(23)	1.376(9)
C(23)–C(24)	1.395(9)
C(24)–C(25)	1.391(8)
C(26)–C(27)	1.378(8)
C(26)–C(31)	1.385(8)
C(27)–C(28)	1.398(9)
C(28)–C(29)	1.365(10)
C(29)–C(30)	1.372(9)
C(30)–C(31)	1.389(9)
C(32)–C(33)	1.384(7)
C(32)–C(37)	1.404(7)
C(33)–C(34)	1.386(8)
C(34)–C(35)	1.376(10)
C(35)–C(36)	1.388(10)
C(36)–C(37)	1.381(8)
C(38)–C(39)	1.376(8)
C(38)–C(43)	1.397(8)
C(39)–C(40)	1.390(8)
C(40)–C(41)	1.374(9)
C(41)–C(42)	1.369(10)
C(42)–C(43)	1.383(8)

(*continued*)

Table 2 (*continued*)

Table 3
Bond angles (°) for compound **9**

Cl(1)–Pt(1)–Cl(2)	172.25(5)
Cl(1)–Pt(1)–P(1)	87.92(4)
Cl(1)–Pt(1)–P(2)	87.25(4)
Cl(2)–Pt(1)–P(1)	92.02(4)
Cl(2)–Pt(1)–P(2)	93.14(4)
P(1)–Pt(1)–P(2)	174.43(5)
Pt(1)–P(1)–C(1)	120.11(16)
Pt(1)–P(1)–C(20)	114.92(15)
Pt(1)–P(1)–C(26)	108.57(16)
C(1)–P(1)–C(20)	99.9(2)
C(1)–P(1)–C(26)	103.4(2)
C(20)–P(1)–C(26)	108.9(2)
Pt(1)–P(2)–C(19)	118.58(15)
Pt(1)–P(2)–C(32)	113.18(16)
Pt(1)–P(2)–C(38)	109.65(16)
C(19)–P(2)–C(32)	101.7(2)
C(19)–P(2)–C(38)	105.0(2)
C(32)–P(2)–C(38)	107.9(3)
C(6)–N(1)–C(7)	126.1(4)
C(8)–N(2)–C(12)	118.5(4)
C(13)–N(3)–C(14)	125.8(4)
P(1)–C(1)–C(2)	121.8(4)
P(1)–C(1)–C(6)	118.6(3)
C(2)–C(1)–C(6)	119.2(4)
C(1)–C(2)–C(3)	120.7(5)
C(2)–C(3)–C(4)	119.5(5)
C(3)–C(4)–C(5)	120.3(5)
C(4)–C(5)–C(6)	120.5(5)
N(1)–C(6)–C(1)	119.3(4)
N(1)–C(6)–C(5)	120.9(4)
C(1)–C(6)–C(5)	119.8(4)
O(1)–C(7)–N(1)	125.4(4)
O(1)–C(7)–C(8)	121.9(4)
N(1)–C(7)–C(8)	112.7(4)
N(2)–C(8)–C(7)	117.2(4)
N(2)–C(8)–C(9)	122.3(4)
C(7)–C(8)–C(9)	120.5(4)
C(33)–C(32)–C(37)	119.0(4)
C(32)–C(33)–C(34)	120.3(5)
C(33)–C(34)–C(35)	120.3(6)
C(34)–C(35)–C(36)	120.4(6)
C(35)–C(36)–C(37)	119.5(6)

(*continued*)

Table 3 (*continued*)

C(32)–C(37)–C(36)	120.6(5)
P(2)–C(38)–C(39)	117.9(4)
C(8)–C(9)–C(10)	118.7(4)
C(9)–C(10)–C(11)	119.1(5)
C(10)–C(11)–C(12)	118.6(5)
N(2)–C(12)–C(11)	122.7(4)
N(2)–C(12)–C(13)	116.5(5)
C(11)–C(12)–C(13)	120.8(4)
O(2)–C(13)–N(3)	124.9(5)
O(2)–C(13)–C(12)	122.6(5)
N(3)–C(13)–C(12)	112.5(4)
N(3)–C(14)–C(15)	120.5(4)
N(3)–C(14)–C(19)	118.9(4)
C(15)–C(14)–C(19)	120.6(4)
C(14)–C(15)–C(16)	119.6(5)
C(15)–C(16)–C(17)	120.7(5)
C(16)–C(17)–C(18)	119.8(5)
C(17)–C(18)–C(19)	120.5(4)
P(2)–C(19)–C(14)	118.7(3)
P(2)–C(19)–C(18)	122.5(3)
C(14)–C(19)–C(18)	118.8(4)
P(1)–C(20)–C(21)	120.7(4)
P(1)–C(20)–C(25)	120.5(4)
C(21)–C(20)–C(25)	118.6(4)
C(20)–C(21)–C(22)	120.8(5)
C(21)–C(22)–C(23)	120.6(5)
C(22)–C(23)–C(24)	119.5(5)
C(23)–C(24)–C(25)	119.4(5)
C(20)–C(25)–C(24)	121.1(5)
P(1)–C(26)–C(27)	123.9(4)
P(1)–C(26)–C(31)	116.4(4)
C(27)–C(26)–C(31)	119.5(5)
C(26)–C(27)–C(28)	119.3(6)
C(27)–C(28)–C(29)	120.5(6)
C(28)–C(29)–C(30)	120.8(6)
C(29)–C(30)–C(31)	119.0(6)
C(26)–C(31)–C(30)	120.9(6)
P(2)–C(32)–C(33)	121.2(4)
P(2)–C(32)–C(37)	119.7(4)
P(2)–C(38)–C(43)	122.9(5)
C(39)–C(38)–C(43)	119.2(5)
C(38)–C(39)–C(40)	120.1(5)
C(39)–C(40)–C(41)	120.4(6)
C(40)–C(41)–C(42)	119.8(5)
C(41)–C(42)–C(43)	120.6(5)
C(38)–C(43)–C(42)	119.9(6)

0.092(1), −0.117(1), −0.110(1) Å, respectively. The P–Pt–P angle of 174.43(5)° and the Cl–Pt–Cl angle of 172.25(5)° differ significantly from 180°.

The platinum phosphorus distances of 2.3212(12) and 2.3196(12) Å fall in the normal range for complexes with *trans* phosphine ligands [7,17]. The Pt–Cl bonds (2.3174(13) and 2.3102(12)) are nearly the same length as the Pt–P bonds and are similar to those usually observed for *trans* chlorine platinum complexes.

The amide group is nearly planar and has a torsion angle for N(1), C(7), C(8), N(2) of −2.9(6)° and for N(3), C(13), C(12), N(2) of 4.1(6)°. However, the two phenyl rings C(1)–C(6) and C(14)–C(19) are not in the plane of the carbonyl group and are positioned *syn* towards each other. The torsion angle for C(7), N(1), C(6), C(5) is −64.7(7)°

Table 4
Final coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms for compound **9**

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Pt(1)	0.11804(1)	0.04525(2)	0.40584(1)	0.0139(1)
Cl(1)	0.05941(3)	0.15353(15)	0.38140(5)	0.0236(4)
Cl(2)	0.17241(3)	−0.09153(13)	0.42558(5)	0.0191(3)
P(1)	0.10594(3)	−0.00341(14)	0.49424(5)	0.0168(3)
P(2)	0.12645(3)	0.11369(14)	0.31720(5)	0.0160(3)
O(1)	0.18889(9)	0.2619(4)	0.61280(14)	0.0224(11)
O(2)	0.22395(9)	0.4047(4)	0.34371(13)	0.0244(11)
N(1)	0.18504(11)	0.0963(5)	0.54173(18)	0.0173(12)
N(2)	0.20414(10)	0.2928(4)	0.47382(16)	0.0156(12)
N(3)	0.20549(11)	0.1865(5)	0.37374(17)	0.0173(12)
C(1)	0.14097(13)	−0.0985(5)	0.54817(19)	0.0168(12)
C(2)	0.13271(14)	−0.2264(6)	0.5727(2)	0.0200(17)
C(3)	0.15838(15)	−0.2881(6)	0.6181(2)	0.0222(17)
C(4)	0.19209(15)	−0.2192(6)	0.6390(2)	0.0221(17)
C(5)	0.20076(14)	−0.0919(6)	0.6146(2)	0.0187(17)
C(6)	0.17560(12)	−0.0312(5)	0.56903(19)	0.0172(14)
C(7)	0.19151(12)	0.2295(5)	0.5652(2)	0.0173(16)
C(8)	0.20140(12)	0.3401(5)	0.5250(2)	0.0169(14)
C(9)	0.20734(14)	0.4850(6)	0.5413(2)	0.0203(16)
C(10)	0.21520(15)	0.5837(5)	0.5026(2)	0.0222(17)
C(11)	0.21800(13)	0.5354(6)	0.4499(2)	0.0212(17)
C(12)	0.21250(12)	0.3879(6)	0.43738(19)	0.0160(14)
C(13)	0.21493(12)	0.3293(6)	0.3800(2)	0.0176(14)
C(14)	0.20334(12)	0.1031(5)	0.32402(18)	0.0147(12)
C(15)	0.23573(13)	0.0698(6)	0.30499(19)	0.0207(16)
C(16)	0.23343(14)	−0.0213(6)	0.2593(2)	0.0242(16)
C(17)	0.19919(14)	−0.0801(6)	0.2318(2)	0.0230(16)
C(18)	0.16663(13)	−0.0407(6)	0.24874(18)	0.0200(12)
C(19)	0.16831(12)	0.0513(6)	0.29504(17)	0.0159(12)
C(20)	0.09808(12)	0.1574(5)	0.53468(19)	0.0161(14)
C(21)	0.09705(14)	0.1461(6)	0.5916(2)	0.0241(17)
C(22)	0.09302(16)	0.2680(7)	0.6228(2)	0.0284(17)
C(23)	0.09031(15)	0.4038(7)	0.5983(2)	0.0302(17)
C(24)	0.09203(18)	0.4177(6)	0.5415(3)	0.033(2)
C(25)	0.09552(14)	0.2935(6)	0.5102(2)	0.0242(17)
C(26)	0.06486(13)	−0.1214(6)	0.4848(2)	0.0208(16)
C(27)	0.03875(15)	−0.1150(7)	0.5180(3)	0.0310(17)
C(28)	0.00954(16)	−0.2164(8)	0.5094(3)	0.043(2)
C(29)	0.00695(16)	−0.3214(7)	0.4688(3)	0.042(2)
C(30)	0.03272(18)	−0.3289(7)	0.4354(3)	0.042(2)
C(31)	0.06180(16)	−0.2283(7)	0.4437(3)	0.0294(17)
C(32)	0.12958(13)	0.3100(5)	0.3090(2)	0.0172(14)
C(33)	0.12288(14)	0.4045(6)	0.3502(2)	0.0254(17)
C(34)	0.12912(16)	0.5524(7)	0.3460(3)	0.0353(19)
C(35)	0.14153(18)	0.6068(7)	0.3004(3)	0.037(2)
C(36)	0.14739(16)	0.5145(7)	0.2578(3)	0.0327(19)
C(37)	0.14189(15)	0.3668(6)	0.2624(2)	0.0241(17)
C(38)	0.08717(12)	0.0480(7)	0.26251(18)	0.0226(14)
C(39)	0.07295(15)	−0.0877(6)	0.2695(2)	0.0272(17)
C(40)	0.04259(16)	−0.1415(8)	0.2296(3)	0.037(2)
C(41)	0.02601(15)	−0.0586(8)	0.1836(2)	0.039(2)
C(42)	0.03975(16)	0.0771(7)	0.1767(2)	0.036(2)
C(43)	0.07061(16)	0.1307(8)	0.2151(2)	0.0341(19)
Cl(3)	0.01703(7)	0.4593(2)	0.20051(9)	0.0830(9)
C(44)	0.(−)	0.3502(11)	0.25(−)	0.059(4)

U_{eq} = 1/3 of the trace of the orthogonalised U tensor.

and for C(13), N(3), C(14), C(15) is 68.1(7)°. The two hydrogens of the amides are hydrogen bonded to the pyridine nitrogen N(2) and to Cl(2) (Table 5). Further intramolec-

Table 5
Hydrogen bonding geometry (Å, °) for compound **9**

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	D–H···A (°)
N(1)–H(1)···Cl(2)	3.243(5)	0.76(5)	2.60(6)	143(6)
N(1)–H(1)···N(2)	2.638(6)	0.76(5)	2.25(6)	112(6)
N(3)–H(3)···Cl(2)	3.200(5)	0.91(5)	2.47(5)	138(4)
N(3)–H(3)···N(2)	2.621(6)	0.91(5)	2.16(5)	111(2)
C(25)–H(25)···Cl(1)	3.359(5)	0.93(5)	2.70(5)	128(4)
C(33)–H(33)···Cl(1)	3.471(5)	1.18(5)	2.63(5)	127(3)
C(5)–H(5)···O(2) [1/2−x, 1/2−y, 1−z]	3.213(6)	0.83(5)	2.39(5)	173(5)
C(15)–H(15)···O(1) [1/2−x, 1/2−y, 1−z]	3.393(6)	0.94(4)	2.47(4)	167(4)
C(16)–H(16)···O(2) [1/2−x, −1/2+y, 1/2+z]	3.289(6)	0.90(5)	2.54(5)	142(4)
C(17)–H(17)···O(1) [x, −y, −1/2−z]	3.278(6)	0.95(4)	2.34(5)	168(4)

ular H bonds are observed between H(25)···Cl(1) and H(33)···Cl(1). Between the molecules weak hydrogen bonding is observed: H(5)···O(2) [1/2−x, 1/2−y, 1−z], H(15)···O(1) [1/2−x, 1/2−y, 1−z], C(16)–H(16)···O(2) [1/2−x, −1/2+y, 1/2−z] and C(17)–H(17)···O(1) [x, −y, −1/2−z] [18].

2.3. X-ray structure of dichlorobis(2-diphenylphosphinoaniline)platinum (12)

The crystal structure of **12** together with the adopted numbering scheme is shown in Fig. 3. The crystallographic data, selected bond distances, selected bond angles and fractional coordinates are collected in Tables 1 and 6–8.

The platinum complex **12** has a square planar geometry in which the nitrogen and phosphorus donor atoms are *cis* to each other due to the *trans* effect. The square planar coordination around Pt is slightly distorted: the P(1)–Pt(1)–P(2), P(1)–Pt(1)–N(1), P(2)–Pt(1)–N(2) and N(1)–Pt(1)–N(2) bond angles are respectively 102.95(4), 84.51(10), 84.07(9) and 88.47(13)°.

The Pt–P distances of 2.2393(11) and 2.2344(11) Å and the Pt–N distances of 2.102(3) and 2.106(3) Å are slightly shorter than found in *cis*-bis(2-diphenylphosphinoaniline) platinum(II) perchlorate (2.245 and 2.12 Å) [7b].

Highly fascinating is the way in which chloroform is incorporated in the crystal packing; each chloride is hydrogen bonded to two protons of amine moieties and to two protons of chloroform. In this way there are four chloroform mole-

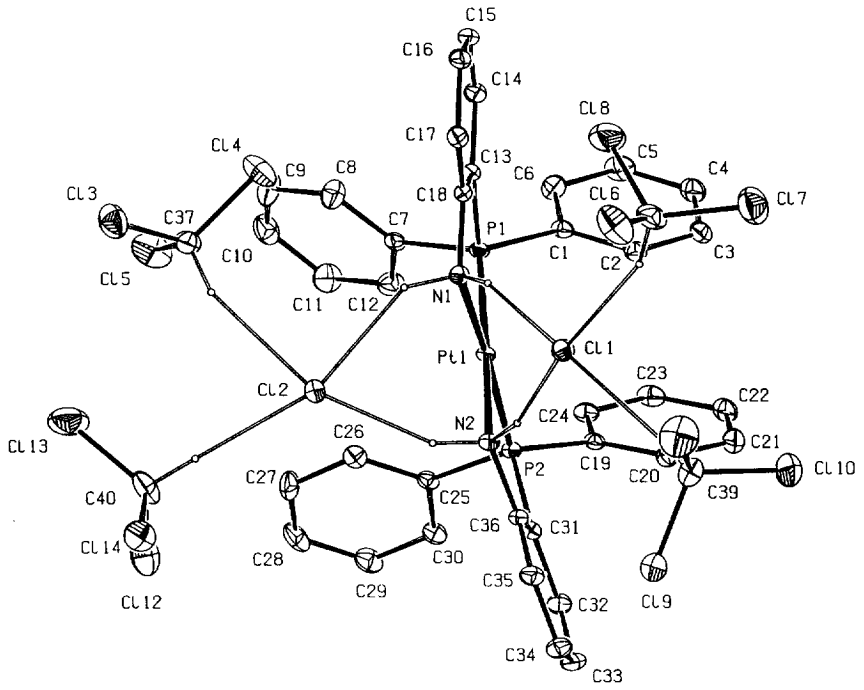


Fig. 3. ORTEP plot of complex **12** with adopted numbering scheme.

Table 6
Bond distances (Å) for compound **12**

Pt(1)–P(1)	2.2393(11)
Pt(1)–P(2)	2.2344(11)
Pt(1)–N(1)	2.102(3)
Pt(1)–N(2)	2.106(3)
P(1)–C(1)	1.814(4)
P(1)–C(7)	1.807(5)
P(1)–C(13)	1.806(4)
P(2)–C(19)	1.812(4)
P(2)–C(25)	1.814(5)
P(2)–C(31)	1.811(5)
N(1)–C(18)	1.462(5)
N(2)–C(36)	1.447(5)
C(1)–C(2)	1.389(7)
C(1)–C(6)	1.390(6)
C(2)–C(3)	1.389(6)
C(3)–C(4)	1.375(6)
C(4)–C(5)	1.376(7)
C(5)–C(6)	1.396(6)
C(7)–C(8)	1.379(7)
C(7)–C(12)	1.396(7)
C(8)–C(9)	1.391(7)
C(9)–C(10)	1.376(8)
C(10)–C(11)	1.382(7)
C(11)–C(12)	1.382(7)
C(13)–C(14)	1.406(6)
C(13)–C(18)	1.385(6)
C(14)–C(15)	1.384(6)
C(15)–C(16)	1.380(6)
C(16)–C(17)	1.387(6)
C(17)–C(18)	1.389(6)
C(19)–C(20)	1.391(7)
C(19)–C(24)	1.384(6)
C(20)–C(21)	1.389(6)
C(21)–C(22)	1.393(6)
C(22)–C(23)	1.387(7)
C(23)–C(24)	1.382(6)
C(25)–C(26)	1.388(6)
C(25)–C(30)	1.395(6)
C(26)–C(27)	1.389(7)
C(27)–C(28)	1.378(7)
C(28)–C(29)	1.373(7)
C(29)–C(30)	1.382(7)
C(31)–C(32)	1.399(6)
C(31)–C(36)	1.388(6)
C(32)–C(33)	1.386(6)
C(33)–C(34)	1.386(6)
C(34)–C(35)	1.381(6)
C(35)–C(36)	1.386(6)

Table 7
Bond angles (°) for compound **12**

P(1)–Pt(1)–P(2)	102.95(4)
P(1)–Pt(1)–N(1)	84.51(10)
P(1)–Pt(1)–N(2)	172.98(9)
P(2)–Pt(1)–N(1)	172.43(10)
P(2)–Pt(1)–N(2)	84.07(9)
N(1)–Pt(1)–N(2)	88.47(13)
Pt(1)–P(1)–C(1)	118.23(15)
Pt(1)–P(1)–C(7)	116.97(14)
Pt(1)–P(1)–C(13)	101.87(15)
C(1)–P(1)–C(7)	106.3(2)
C(1)–P(1)–C(13)	106.1(2)
C(7)–P(1)–C(13)	106.1(2)
Pt(1)–P(2)–C(19)	118.48(15)
Pt(1)–P(2)–C(25)	113.81(15)
Pt(1)–P(2)–C(31)	102.06(14)
C(19)–P(2)–C(25)	109.1(2)
C(19)–P(2)–C(31)	106.8(2)
C(25)–P(2)–C(31)	105.2(2)
Pt(1)–N(1)–C(18)	116.7(2)
Pt(1)–N(2)–C(36)	117.4(2)
P(1)–C(1)–C(2)	118.3(3)
P(1)–C(1)–C(6)	120.9(4)
C(2)–C(1)–C(6)	120.7(4)
C(1)–C(2)–C(3)	119.3(4)
C(2)–C(3)–C(4)	120.4(4)
C(3)–C(4)–C(5)	120.3(4)
C(4)–C(5)–C(6)	120.5(4)
C(1)–C(6)–C(5)	118.8(4)
P(1)–C(7)–C(8)	121.3(3)
P(1)–C(7)–C(12)	119.9(3)
C(8)–C(7)–C(12)	118.7(4)
C(7)–C(8)–C(9)	119.8(5)
C(8)–C(9)–C(10)	120.8(5)
C(9)–C(10)–C(11)	120.1(5)
C(10)–C(11)–C(12)	119.0(5)
C(7)–C(12)–C(11)	121.5(5)
P(1)–C(13)–C(14)	124.0(3)
P(1)–C(13)–C(18)	116.8(3)
C(14)–C(13)–C(18)	119.2(4)
C(13)–C(14)–C(15)	119.7(4)
C(14)–C(15)–C(16)	120.1(4)
C(15)–C(16)–C(17)	121.0(4)
C(16)–C(17)–C(18)	118.8(4)
N(1)–C(18)–C(13)	118.7(4)
N(1)–C(18)–C(17)	120.1(4)
C(13)–C(18)–C(17)	121.2(4)
P(2)–C(19)–C(20)	118.1(3)
P(2)–C(19)–C(24)	121.0(4)
C(20)–C(19)–C(24)	120.5(4)
C(19)–C(20)–C(21)	119.7(4)
C(20)–C(21)–C(22)	119.9(4)
C(21)–C(22)–C(23)	119.9(4)
C(22)–C(23)–C(24)	120.4(4)
C(19)–C(24)–C(23)	119.7(4)
P(2)–C(25)–C(26)	118.0(3)
P(2)–C(25)–C(30)	122.0(4)
C(26)–C(25)–C(30)	119.6(4)
C(25)–C(26)–C(27)	119.6(4)
C(26)–C(27)–C(28)	120.4(4)
C(27)–C(28)–C(29)	120.1(5)
C(28)–C(30)–C(29)	120.3(5)
C(25)–C(30)–C(29)	120.0(4)
P(2)–C(31)–C(32)	124.4(3)
P(2)–C(31)–C(36)	116.5(3)
C(32)–C(31)–C(36)	119.0(4)
C(31)–C(32)–C(33)	119.8(4)
C(32)–C(33)–C(34)	120.5(4)
C(33)–C(34)–C(35)	120.0(4)
C(34)–C(35)–C(36)	119.8(4)
N(2)–C(36)–C(31)	118.5(4)
N(2)–C(36)–C(35)	120.6(4)
C(31)–C(36)–C(35)	120.9(4)

cules hydrogen bonded to platinum complex **12**. The hydrogen bond distances are collected in Table 9. This structural feature has attractive implications for the design of supramolecular platinum based systems.

Table 8
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for compound **12**

Atom	x	y	z	U_{eq} (Å)
Pt(1)	0.31934(1)	0.11617(1)	0.23560	0.0161(1)
P(1)	0.44867(10)	0.21016(9)	0.27754(4)	0.0181(3)
P(2)	0.12984(10)	0.27345(9)	0.23141(4)	0.0171(3)
N(1)	0.4830(3)	−0.0479(3)	0.2362(2)	0.0202(12)
N(2)	0.2175(3)	0.0073(3)	0.19594(15)	0.0198(12)
C(1)	0.4949(4)	0.3513(4)	0.2459(2)	0.0217(12)
C(2)	0.5078(4)	0.3638(4)	0.1883(2)	0.0247(12)
C(3)	0.5506(4)	0.4676(4)	0.1628(2)	0.0306(12)
C(4)	0.5809(5)	0.5565(4)	0.1942(2)	0.0341(14)
C(5)	0.5675(5)	0.5444(4)	0.2513(2)	0.0383(16)
C(6)	0.5242(5)	0.4413(4)	0.2780(2)	0.0310(12)
C(7)	0.3895(4)	0.2460(4)	0.3514(2)	0.0221(12)
C(8)	0.4465(5)	0.1673(5)	0.3911(2)	0.0367(17)
C(9)	0.3990(6)	0.1980(6)	0.4476(2)	0.050(2)
C(10)	0.2952(6)	0.3061(5)	0.4645(2)	0.0431(16)
C(11)	0.2344(5)	0.3843(5)	0.4253(2)	0.0401(17)
C(12)	0.2817(5)	0.3536(5)	0.3692(2)	0.0340(14)
C(13)	0.6102(4)	0.0882(4)	0.2715(2)	0.0187(12)
C(14)	0.7325(4)	0.1064(4)	0.2862(2)	0.0249(12)
C(15)	0.8508(4)	0.0064(4)	0.2807(2)	0.0254(12)
C(16)	0.8496(4)	−0.1100(4)	0.2598(2)	0.0264(12)
C(17)	0.7305(4)	−0.1294(4)	0.2444(2)	0.0251(12)
C(18)	0.6110(4)	−0.0297(4)	0.2510(2)	0.0189(12)
C(19)	0.1532(4)	0.4216(4)	0.1992(2)	0.0199(12)
C(20)	0.1818(4)	0.4259(4)	0.1411(2)	0.0255(12)
C(21)	0.2170(5)	0.5323(4)	0.1150(2)	0.0312(12)
C(22)	0.2260(4)	0.6328(4)	0.1471(2)	0.0314(14)
C(23)	0.1971(4)	0.6273(4)	0.2050(2)	0.0294(14)
C(24)	0.1589(4)	0.5228(4)	0.2311(2)	0.0245(12)
C(25)	0.0091(4)	0.3084(4)	0.2976(2)	0.0206(12)
C(26)	0.0243(4)	0.2194(4)	0.3398(2)	0.0259(12)
C(27)	−0.0748(5)	0.2366(5)	0.3889(2)	0.0333(16)
C(28)	−0.1871(5)	0.3416(5)	0.3960(2)	0.0384(16)
C(29)	−0.2021(5)	0.4299(5)	0.3544(2)	0.0342(16)
C(30)	−0.1055(4)	0.4138(4)	0.3050(2)	0.0257(12)
C(31)	0.0411(4)	0.2034(4)	0.1874(2)	0.0194(12)
C(32)	−0.0781(4)	0.2693(4)	0.1674(2)	0.0245(12)
C(33)	−0.1382(4)	0.2065(4)	0.1340(2)	0.0274(12)
C(34)	−0.0827(4)	0.0781(4)	0.1212(2)	0.0292(12)
C(35)	0.0345(4)	0.0123(4)	0.1411(2)	0.0258(12)
C(36)	0.0959(4)	0.0750(4)	0.1740(2)	0.0189(12)
Cl(3)	0.43625(15)	0.61096(14)	0.44278(7)	0.0540(5)
Cl(4)	0.56044(13)	0.78930(13)	0.37461(7)	0.0531(5)
Cl(5)	0.3240(2)	0.8817(2)	0.46290(7)	0.0614(5)
C(37)	0.4037(5)	0.7629(5)	0.4124(2)	0.0342(14)
Cl(6)	0.8174(2)	0.5402(2)	0.04097(8)	0.0690(6)
Cl(7)	0.8703(2)	0.7671(2)	−0.01491(7)	0.0633(6)
Cl(8)	0.8854(2)	0.7328(2)	0.10137(7)	0.0697(7)
C(38)	0.8007(5)	0.7043(6)	0.0479(2)	0.0439(18)
Cl(9)	0.79604(14)	0.1858(2)	−0.00827(6)	0.0536(5)
Cl(10)	0.5795(2)	0.08125(15)	0.05703(6)	0.0557(5)
Cl(11)	0.5165(2)	0.3412(2)	0.02048(8)	0.0713(6)
C(39)	0.6181(5)	0.1860(5)	0.0039(2)	0.0362(16)
Cl(12)	0.1802(2)	0.07985(14)	0.57593(6)	0.0583(5)
Cl(13)	−0.0377(2)	0.2558(2)	0.52983(7)	0.0761(8)
Cl(14)	0.06593(14)	0.33557(13)	0.62062(6)	0.0472(4)
C(40)	0.0291(6)	0.2061(6)	0.5912(2)	0.0481(19)
Cl(1)	0.47686(10)	0.83831(10)	0.12044(4)	0.0261(3)
Cl(2)	0.22396(11)	0.85833(11)	0.30867(4)	0.0310(3)

U_{eq} = 1/3 of the trace of the orthogonalised U tensor.

3. Conclusions

New polydentate ligands based on 2-diphenylphosphinoaniline with rigid bridging groups have been synthesised. Ligand **3**, with a phenyl bridging group gave dinuclear palladium complex **8** by the reaction with Pd(COD)MeCl but did not form well defined mononuclear complexes, probably due to bridging CH in the phenyl group. In ligand **7**, the phosphorus atoms are positioned close to each other because of hydrogen bonding between the two amide hydrogens and the pyridine nitrogen. Therefore, mononuclear complexes of **7** are obtained with Ni, Pd and Pt. The crystal structure of mononuclear platinum complex **9** and ^{31}P NMR data proved that the two phosphorus atoms are coordinating *trans* to platinum. In contrast to **9**, nickel is coordinated to ligand **7** in a square planar mode with *cis* coordination of the phosphines to nickel.

4. Experimental

4.1. General methods

The synthesis of the complexes was performed under an atmosphere of argon. Dichloromethane, hexane and pentane were distilled under nitrogen atmosphere from P_2O_5, toluene and benzene from sodium and tetrahydrofuran from sodium benzophenone. Pyridine was distilled from and stored on KOH. 2-Diphenylphosphinoaniline [5], bis(acetonitrile)-dichloropalladium, bis(acetonitrile)dichloroplatinum [19] and chloro(1,5-cyclooctadiene)methylpalladium [20] were prepared by literature procedures. Isophthalaldehyde, pyridinedicarbonyl dichloride and isophthaloyl dichloride were obtained from Aldrich and used without further purification. ^{1}H, ^{31}P and ^{13}C NMR were recorded at 200, 81 and 50 MHz with a Varian Gemini 200 FT NMR spectrometer. Chemical shifts are reported in ppm and referenced to the residual deuterated solvent signals for ^{1}H and ^{13}C and external triphenylphosphate (δ −18) for ^{31}P. Electron ionisation mass spectra (EI-MS) were performed on a AEI-MS-902 spectrometer. Elemental analyses were determined in the Microanalytical Department of the University of Groningen.

Caution! $Ni(ClO_4)_2$ is potentially explosive and should be handled with care.

4.2. Synthesis

4.2.1. Synthesis of 1,3-bis[N,N'-(2-diphenylphosphino)phenylformimidoyl]benzene (3)

To a solution of isophthalaldehyde (0.24 g, 1.8 mmol) in toluene (50 ml) was added 2-diphenylphosphinoaniline (1 g, 3.6 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The solution was refluxed for 6 h under Dean–Stark conditions. The solvent was evaporated yielding a yellow foam, which was crystallised from CH_2Cl_2/hexane. Yield 0.9 g (77%). M.p. 203°C. ^{31}P NMR ($CDCl_3$): δ −14.1. ^{1}H

Table 9
Hydrogen bonding geometry (Å, °) for compound **12**

	D–H	H···A	D···A	D–H···A
N(1)–H(1A)···Cl(1) [x, −1+y, z]	0.88(4)	2.30(4)	3.132(5)	158(4)
N(1)–H(1B)···Cl(2) [x, −1+y, z]	0.99(7)	2.38(7)	3.227(4)	143(5)
N(2)–H(2A)···Cl(1) [x, −1+y, z]	0.97(5)	2.16(6)	3.094(4)	163(5)
N(2)–H(2B)···Cl(2) [x, −1+y, z]	1.00(5)	2.22(5)	3.140(4)	153(4)
C(37)–H(37)···Cl(2)	0.981(7)	2.465(5)	3.368(5)	152.8(5)
C(38)–H(38)···Cl(1)	0.980(8)	2.466(5)	3.390(6)	157.0(5)
C(39)–H(39)···Cl(1) [1−x, 1−y, −z]	0.979(7)	2.436(5)	3.380(5)	161.8(5)
C(40)–H(40)···Cl(2) [−x, 1−y, 1−z]	0.980(8)	2.400(6)	3.369(6)	169.7(6)

NMR ($CDCl_3$): δ 8.16 (s, 2H, HC=N), 7.82–7.74 (m, 3H, ArH), 7.45–7.27 (m, 23H, ArH), 7.16 (t, J=7.0 Hz, 2H), 7.12–7.0 (m, 2H, ArH), 6.90–6.84 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 158.8 (CH), 153.7 (d, $^1J_{PC}$=17.5 Hz, C), 136.7 (d, $^2J_{PC}$=10.3, C), 136.2 (C), 134.1 (d, $^1J_{PC}$=20.2 Hz, CH), 132.8 (d, $^2J_{PC}$=11.8 Hz, C), 132.5 (CH), 130.8 (CH), 129.8 (CH), 129.7 (CH), 128.6 (CH), 128.4 (d, $^2J_{PC}$=8.4 Hz, CH), 128.2 (d, $^3J_{PC}$=7.6, CH), 126.0 (CH), 116.9 (CH). *Anal.* Calc. for $C_{44}H_{34}N_2P_2$: C, 80.97; H, 5.25; N, 4.28; P, 9.49. Found: C, 80.95; H, 5.25; N, 4.28; P, 9.51%.

4.2.2. Synthesis of bis[N,N'-(2-diphenylphosphinophenyl)]-1,3-benzenedicarboxamide (6)

To a solution of 2-diphenylphosphinoaniline (1 g, 3.6 mmol) in THF (10 ml) was added pyridine (0.9 ml, 10.8 mmol) and 1,3-benzenedicarbonyl dichloride (366 mg, 1.8 mmol) in THF (2 ml). The reaction mixture was stirred for 1 h, filtered and evaporated yielding a white sticky solid. The solid was dissolved in CH_2Cl_2 and extracted with 5% HCl (3×30 ml). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The solid residue was crystallised from CH_2Cl_2/hexane yielding **6** as a white powder. Yield 0.89 g (72%). M.p. 184°C. ^{31}P NMR ($CDCl_3$): δ −20.0. ^1H NMR ($CDCl_3$): δ 8.77 (d, J=8 Hz, 2H, NH), 8.35 (m, 2H, ArH), 8.09 (s, 1H, ArH), 7.72 (m, 2H, ArH), 7.51–7.26 (m, 23H, ArH), 7.12 (t, J=8 Hz, 2H, ArH), 6.99 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 164.2 (C), 140.7 (d, $^1J_{PC}$=17.1 Hz, C), 135.3 (C), 134.0 (d, $^2J_{PC}$=6.1 Hz, C), 133.8 (CH), 133.6 (CH), 130.3 (CH), 129.9 (CH), 129.3 (CH), 129.0 (CH), 128.8 (d, $^2J_{PC}$=8.6 Hz, CH), 127.0 (d, $^1J_{PC}$=9.8 Hz, C), 125.6 (CH), 125.1 (CH), 122.1 (CH). *Anal.* Calc. for $C_{44}H_{34}N_2O_2P_2$: C, 76.78; H, 5.01; N, 4.09; P, 9.05. Found: C, 76.78; H, 5.00; N, 4.07; P, 9.03%.

4.2.3. Synthesis of bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide (7)

To a solution of 2-diphenylphosphinoaniline (1 g, 3.6 mmol) in THF (10 ml) was added pyridine (0.9 ml, 10.8 mmol) and 2,5-pyridinedicarbonyl dichloride (368 mg, 1.8 mmol) in THF (2 ml). The reaction mixture was stirred for 1 h, filtered and evaporated yielding a white sticky solid. The solid was solved in CH_2Cl_2 and extracted with 20% NH_4Cl (5×30 ml). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The solid residue was crystallised from CH_2Cl_2/hexane yielding **7** as a white powder. Yield 0.67 g (54%). M.p. 224°C. ^{31}P NMR ($CDCl_3$): δ −19.9. ^1H NMR ($CDCl_3$): δ 10.60 (s, 2H, NH), 8.27 (d, 2H, ArH), 8.17 (br d, 2H, ArH), 7.99 (m, 1H, ArH), 7.48 (t, J=7 Hz, 2H, ArH), 7.27–7.13 (m, 22H, ArH), 6.97 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 161.3 (C), 148.4 (C), 140.3 (t, $^1J_{PC}$=19.5 Hz, C), 139.0 (CH), 134.8 (t, $^2J_{PC}$=7.2 Hz), 133.7 (t, $^2J_{PC}$=20 Hz, CH), 130.0 (CH), 129.8 (t, $^1J_{PC}$=12 Hz, C), 128.9 (CH), 128.5 (t, $^3J_{PC}$=7.3 Hz, CH), 125.7 (CH), 125.0 (CH), 123.6 (CH). 1 CH was not resolved due to overlap. *Anal.* Calc. for $C_{43}H_{33}N_3O_2P_2$: C, 75.26; H, 4.85; N, 6.13; P, 9.03. Found: C, 75.08; H, 4.88; N, 6.28; P, 9.14%.

4.2.4. Synthesis of dichlorodimethyl{1,3-bis[N,N'-(2-diphenylphosphino)phenylformimidoyl]benzene}-dipalladium (8)

A solution of **3** (200 mg, 0.31 mmol) and Pd(Me)Cl(COD) (162.3 mg, 0.62 mmol) in THF (2 ml) was stirred for 1 h at room temperature. The white precipitate was filtered off and crystallised from CH_2Cl_2/pentane. Yield 186 mg (62%). ^{31}P NMR: δ 35.0. ^1H NMR ($CDCl_3$): δ 10.10 (s, 1H, ArH), 8.87 (s, 2H, HC=N), 8.67 (dd, J=8, 1.5 Hz, 2H, ArH), 7.67–7.01 (m, 29H, ArH), 0.92 (d, J=3 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.5(CH), 156.7 (d, $^2J_{PC}$=16.0 Hz, C), 135.6 (CH), 135.2 (CH), 133.4 (d, $^2J_{PC}$=12.6 Hz, CH), 133.1 (CH), 132.7 (C), 131.9 (CH), 131.3 (d, $^4J_{PC}$=2.3 Hz, CH), 130.5 (d, $^1J_{PC}$=47.6, C), 128.2 (d, $^2J_{PC}$=6.5 Hz, CH), 128.0 (d, $^1J_{PC}$=53 Hz, C), 127.9 (CH), 119.5 (d, $^3J_{PC}$=7.6 Hz, CH), −0.9 (CH_3). *Anal.* Calc. for $C_{46}H_{40}Cl_2N_2P_2Pd_2 \cdot CH_2Cl_2$: C, 55.35; H, 4.10; N, 2.78. Found: C, 54.87; H, 4.15; N, 2.77%.

4.2.5. Synthesis of dichloro{bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}-platinum (9)

A solution of **7** (100 mg, 0.147 mmol) and bis(acetonitrile)dichloroplatinum (50.8 mg, 0.147 mmol) in CH_2Cl_2 (2 ml) was stirred for 1 h at room temperature. The mixture was poured in hexane (20 ml) and the resulting yellow solid was filtered off and crystallised from CH_2Cl_2/pentane. Yield: 72 mg (52%). ^{31}P NMR ($CDCl_3$): δ 15.4, J(^{195}Pt–

^{31}P) = 2457 Hz. ^{1}H NMR ($CDCl_3$): δ 11.05 (s, 2H, NH), 8.29 (d, J = 8 Hz, 2H, ArH), 8.04 (m, 1H, ArH), 7.84–7.44 (m, 26H, ArH), 7.07–6.94 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 161.5 (C), 148.4 (C), 139.3 (t, $^{1}J_{PC}$ = 6.7 Hz), 138.8 (CH), 135.2 (t, $^{2}J_{PC}$ = 12.6 Hz, CH), 132.9 (CH), 131.7 (CH), 131.0 (CH), 128.2 (t, $^{3}J_{PC}$ = 10.7 Hz, CH), 126.8 (CH), 126.7 (t, $^{1}J_{PC}$ = 59 Hz, C) 125.9 (t, $^{3}J_{PC}$ = 8.0 Hz, CH), 125.4 (CH), 124.5 (t, $^{1}J_{PC}$ = 60 Hz, C). *Anal.* Calc. for $C_{43}H_{33}Cl_2N_3O_2P_2Pt \cdot CH_2Cl_2$: C, 50.98; H, 3.40; N, 4.05; Cl, 13.68. Found: C, 50.97; H, 3.48; N, 4.12; Cl, 13.48%.

4.2.6. Synthesis of dichloro{bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinecarboxamide}palladium (10)

A solution of **7** (100 mg, 0.147 mmol) and bis(acetonitrile)dichloropalladium (37.8 mg, 0.147 mmol) in CH_2Cl_2 (2 ml) was stirred for 1 h at room temperature. The mixture was poured in hexane (20 ml) and the resulting yellow solid was filtered off and crystallised from CH_2Cl_2/pentane. Yield: 55 mg (43%). ^{31}P NMR ($CDCl_3$): δ 19.4. ^{1}H NMR ($CDCl_3$): δ 11.11 (s, 2H, NH), 8.30 (d, J = 8 Hz, 2H, ArH), 8.09 (m, 1H, ArH), 7.80–7.21 (m, 26H, ArH), 7.17–6.96 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 161.5 (C), 148.3 (C), 139.3 (C), 139.0 (CH), 135.1 (t, $^{2}J_{PC}$ = 13.0 Hz, CH), 132.7 (CH), 131.8 (CH), 130.9 (CH), 128.2 (t, $^{3}J_{PC}$ = 10.7 Hz, CH), 127.5 (CH), 127.4 (t, $^{1}J_{PC}$ = ±50 Hz, C) 126.4 (t, $^{3}J_{PC}$ = 7 Hz, CH), 125.2 (CH) > 1 CH was not resolved. *Anal.* Calc. for $C_{43}H_{33}Cl_2N_3O_2P_2Pd \cdot CH_2Cl_2$: C, 59.85; H, 3.85; N, 4.87; Cl, 8.23. Found: C, 60.01; H, 3.90; N, 4.78; Cl, 8.46%.

4.2.7. Synthesis of {bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamidato}nickel (11)

To a solution of **7** (500 mg, 0.73 mmol) in CH_2Cl_2 (10 ml) was added $Ni(ClO_4)_2 \cdot 6H_2O$ (267 mg, 0.73 mmol) and NaOH (58.4 mg, 1.46 mmol). The mixture was stirred for 1 h at room temperature and the solvent was evaporated. Crystallisation from CH_2Cl_2/EtOH yielded red needles. Yield: 372 mg (68%). ^{31}P NMR ($CDCl_3$): δ 5.9. ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J = 8 Hz, 2H, ArH), 7.90 (t, J = 8, 1H, ArH), 7.86 (m, 4H, ArH), 7.55 (d, J = 8, 2H, ArH), 7.30–7.07 (m, 16H, ArH), 6.93–6.75 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$): δ 167.7 (C), 152.8 (t, C), 150.1 (C), 139.9 (CH), 133.8 (t, CH), 133.7 (t, CH), 133.0 (t, C), 132.2 (CH), 131.7 (t, C), 132.2 (CH), 130.5 (CH), 129.8 (CH), 129.5 (C) 129.1 (CH), 128.2 (CH), 128.1 (CH), 124.7 (CH), 123.8 (CH), 123.3 (CH). *Anal.* Calc. for $C_{43}H_{33}N_3O_2P_2Ni$: C, 69.39; H, 4.47; N, 5.64. Found: C, 67.97; H, 4.52; N, 5.44%. m/z (ES): 741 (M^+).

4.2.8. Synthesis of dichlorobis(2-diphenylphosphinoaniline)platinum (12)

To a solution of 2-diphenylphosphinoaniline (**1**) (150 mg, 0.54 mmol) in $CHCl_3$ (2 ml) was added $(CH_3CN)_2PtCl_2$ (94 mg, 0.27 mmol). The mixture was stirred for 1 h at room temperature and the solvent was evaporated and the resulting light yellow solid was crystallised from CH_2Cl_2/pentane. Crystals suitable for X-ray analysis were obtained by crystallisation from $CHCl_3$/hexane. Yield: 127 mg (63%). ^{31}P NMR ($CDCl_3$): δ 25.7, $J(^{195}Pt–^{31}P)$ = 3349 Hz. ^{1}H NMR ($CDCl_3$): δ 9.68 (s, 4H, NH_2), 7.83 (m, 4H, ArH), 7.52–7.10 (m, 20H, ArH). ^{13}C NMR ($CDCl_3$): δ 147.4 (C), 134.1 (CH), 133.1 (t, $^{2}J_{PC}$ = 11.8 Hz, CH), 132.2 (CH), 132.1 (CH), 130.2 (d, $^{1}J_{PC}$ = 64.9 Hz, C), 129.0 (t, $^{3}J_{PC}$ = 11.8 Hz, CH), 128.3 (t, $^{3}J_{PC}$ = 7.6 Hz, CH), 127.0 (t, $^{2}J_{PC}$ = 14.1 Hz, CH), 125.2 (d, $^{1}J_{PC}$ = 67.1 Hz, C). *Anal.* Calc. for $C_{36}H_{32}Cl_2N_2P_2Pt \cdot 0.15CH_2Cl_2$: C, 51.35; H, 3.85; N, 3.31. Found: C, 51.26; H, 4.02; N, 3.34%.

4.3. Crystal structures

4.3.1. X-ray structure determination of dichloro{bis[N,N'-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}platinum (9)

A parallelepiped, yellow coloured crystal was transferred to the goniostat and cooled to 130 K by using an on-line liquid nitrogen cooling system [21] mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 [22] setting angles of 22 reflections with $16.33 < \theta < 19.05°$. The unit-cell parameters were checked for higher lattice symmetry [23]. Crystal data and details on data collection and refinement are presented in Table 1. The net intensities of the data were corrected for the scale variation, Lorentz and polarisation effects, and for absorption (with the program DIFABS [24]). The structure was solved by Patterson methods and difference Fourier techniques (DIRDIF [25]). The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ [26]). Subsequent difference Fourier summations showed density which could be correlated to the solvent molecule of dichloromethane with the carbon atom on a special position (two-fold axis). Following the inclusion of the positional parameters of the asymmetric part of the solvent molecule, the remainder of the structure refined smoothly. Following the anisotropic refinement of the heavy atoms, the hydrogen atoms were located in subsequent difference Fourier maps and refined for their positional parameters and isotropic thermal displacement parameters. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at R_F = 0.031 (wR = 0.029). A final difference Fourier map was essentially featureless with the highest peaks in the vicinity of the heavy atoms. Neutral scattering factors were used [27] and anomalous dispersion factors [28] were included in F_c. Geometrical calculations and illustrations were performed with PLATON [29]. All calculations were carried out on a HP9000/735 computer.

*4.3.2. X-ray structure determination of dichloro-bis(2-diphenylphosphinoaniline)platinum (**12**)*

A colourless, plate-shaped crystal was glued to the tip of a glass fibre and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centred reflections (SET4 [22]) in the range $11.56 < \theta < 13.91°$. The unit-cell parameters were checked for the presence of higher lattice symmetry [23]. Crystal data and details on data collection and refinement are presented in Table 1. Data were corrected for L_p effects and the observed linear decay. An analytical absorption correction was applied (ABSORB implemented in PLATON [29]). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92 [25]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93 [30]); no observance criterium was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms, except for the amine hydrogen atoms, which were located on a difference Fourier map and subsequently included in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The amine hydrogen atoms were refined with an individual isotropic displacement parameter; the other hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.2. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography [31]. Geometrical calculations and illustrations were performed with PLATON [29]. All calculations were performed on a DECstation 5000/125.

5. Supplementary material

Further details of the structure determinations, including atomic coordinates, bond lengths and angles and thermal parameters for **9** and **12** (100 pages) are available from the authors on request.

Acknowledgements

This work was supported in part (A.L.S.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). Financial support by Shell Research B.V. (E.K. van den B. and B.L.F.) is gratefully acknowledged. We thank Dr P.H.M. Budzelaar for valuable discussions.

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